

<Research Paper>

Electrochemical Study on Energy Potential Levels with Pyrene Molecule

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Abstract: Pyrene based molecule has been synthesized through the reaction of pyrene-1-carboxaldehyde and 4-phenylthiosemicarbazide in this research. The pyrene based molecule showed specific optical properties such as absorption and emission changes after mixing with fluoride in DMSO. The phenomenon is induced by the interaction of the molecule and fluoride. This interaction may affect to electron distributions and potential energy levels. In this regard, synthesized pyrene based molecule has been investigated for its electron distributions and HOMO/LUMO energy levels depending on interaction with fluoride. The absorption measurement, cyclicvoltammograms and computational method were investigated to calculate and compare energy potential levels.

Keywords: pyrene, fluoride, absorption, emission, HOMO, LUMO, cyclicvoltammogram

1. Introduction

Electrochemistry has been studied with the theory and experimental method in analytical chemistry area¹⁾. In this area, cyclic voltammetry has been the most investigated due to efficiency of obtaining data about analyte¹⁾. In this approach, HOMO/LUMO energy levels can be calculated. The HOMO/LUMO energy levels were affected by molecular orbital and identifications of electron transition. These levels are useful to understand the relationship between proton transfer functions/unshared pair/empty orbital interactions and HOMO/LUMO potential energy levels, also helpful to estimate quantum chemistry calculation and redox/oxidation potential determination²⁻⁴⁾.

Pyrene fluorophore is one of the most famous fluorophore because a singlet excited state with showing high emission quantum yields, long life time and also interesting diverse photophysical properties⁵⁾.

In addition, thiourea is one of the typical investigated units for detecting F⁻ by deprotonation of NH-

fragments in the moiety⁶⁻¹²⁾.

In this work, pyrene based molecule has been synthesized through the reaction of pyrene-1-carboxaldehyde and 4-phenylthiosemicarbazide. The pyrene based molecule showed specific optical properties such as absorption and emission changes after interaction with F⁻. We expected that electrochemical behavior may be affected by this interaction. According to this, the pyrene based molecule has been investigated for its electron distributions and HOMO/LUMO energy levels after and before interaction with F⁻ using absorption measurement, cyclicvoltammograms and computational method.

2. Experimental

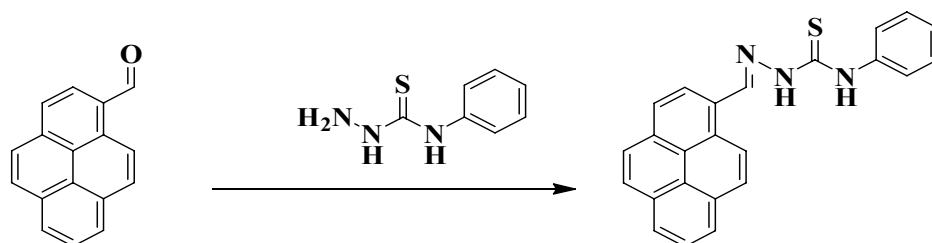
2.1 Pyrene Based Molecule

1-pyrene carboxaldehyde (0.230g, 1mmol) and 4-phenylthiosemicarbazide (0.167g, 1mmol) in 30mL EtOH were mixed and refluxed under nitrogen atmosphere. After 4hrs, the yellow precipitate was filtered and further purified by column chromatography on silicagel (Hexane : EA = 3 : 1). Yield : 57%. ¹H NMR (600 MHz, DMSO-*d*₆) : 11.94 (s, 1H), 10.33 (s, 1H),

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Scheme 1. The synthetic method for pyrene based molecule.

9.40 (s, 1H), 9.08-9.07 (d, 1H), 8.50-8.49 (d, 1H), 8.38-8.34 (q, 4H), 8.29-8.24 (q, 2H), 8.14-8.12 (t, 1H), 7.65-7.63 (d, 2H), 7.43-7.40 (t, 2H), 7.26-7.23 (t, 1H). $^{13}\text{C-NMR}$ (600 MHz, $\text{DMSO-}d_6$) : 175.4, 140.7, 139.1, 132.0, 130.9, 130.1, 128.9, 128.7, 128.3, 128.1, 127.5, 126.7, 126.6, 126.1, 125.9, 125.8, 125.4, 125.1, 124.3, 124.0, 123.8, 121.5. ESI-MS : 380.0 [Pyrene based molecule + H] $^+$.

2.2 Measurements

All reagents and solvents, used for the synthesis of pyrene based dye, were purchased from Aldrich company and used without further purification. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on an NMR spectrometer BRUKER AVNACE IIII 600 operating at 600 MHz. ESI-Mass (Electrospray Ionization) were recorded on a JEOL MStation [JMS-700] Mass Spectrometer. Absorption and fluorescent spectra were measured with Agilent 8453 and Shimadzu RF-5301PC fluorescent spectrophotometer, respectively. Electron density distributions and energy potentials were calculated with DMol 3 of *Material Studio 4.3* package.

3. Results and Discussion

To investigate the change of optical properties depending on the interaction between pyrene based molecule and F^- , absorption and fluorescence spectra were measured. In Figure 1, the only pyrene based molecule (10 μM) showed the band with two peaks at 390nm and 411nm. After mixing with F^- (30 μM) and pyrene based molecule (10 μM) in DMSO, the shape of the spectra was changed. The absorption peaks at 390nm and 411nm decreased and new band centered at 475nm appeared. The fluorescence spectra also showed similar changes.

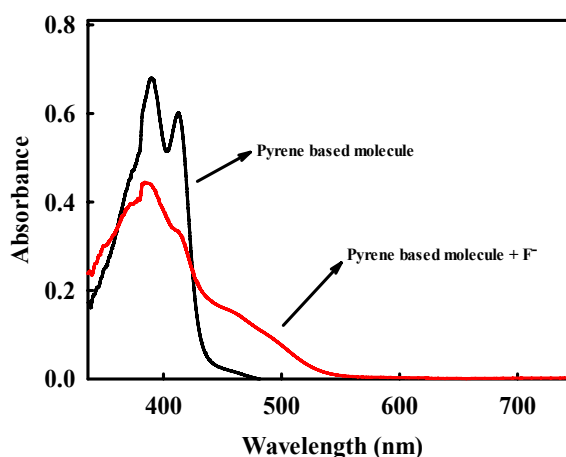


Figure 1. UV-Vis spectra of pyrene based molecule (10 μM) upon addition of F^- ion (30 μM) in DMSO.

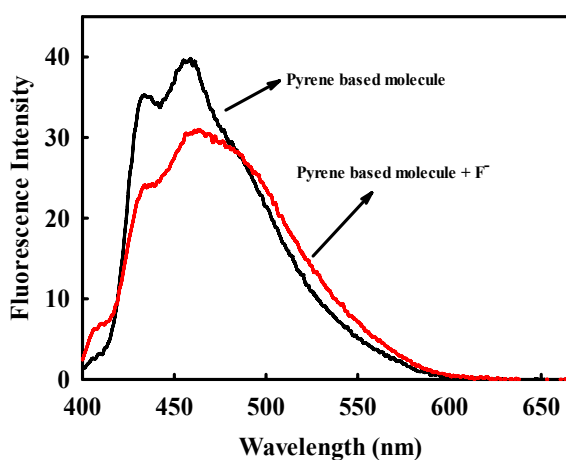


Figure 2. Fluorescence spectra of pyrene based molecule (10 μM) upon addition of F^- ion (30 μM) in DMSO.

As shown in Figure 2, the fluorescence spectrum of pyrene based molecule appeared with showing two peaks such as 390nm and 411nm. However, new band centered at 475nm appeared and initial two peaks decreased after the addition of F^- . These absorption and emission changes may be induced by

the interaction between pyrene based molecule and F^- . The binding ratio between pyrene based molecule and F^- is also important to understand the interaction between pyrene based molecule and F^- . In this regard, the Job's plot method was investigated in Figure 3^{13,14}. For the measurement of Job's plot method, various molar ratios between pyrene based molecule and F^- (1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, 9:1, 10:0) in DMSO were prepared. Each plot was recorded for fluorescence intensity at 387nm. The relationship between maximum absorption peaks versus various mole fractions was recorded as shown in Figure 3. From the findings, the highest fluorescence intensity was obtained, indicating that mole fraction was close to 50%. The result indicated 1:1 complex stoichiometry composition of pyrene based molecule + F^- .

The interaction between pyrene based molecule and F^- can be explained by structural change of the molecule.

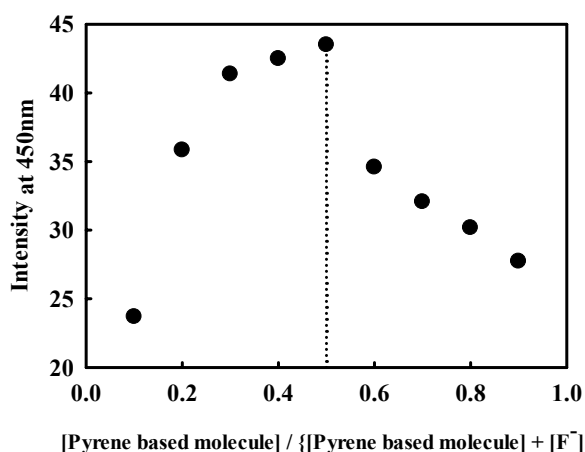
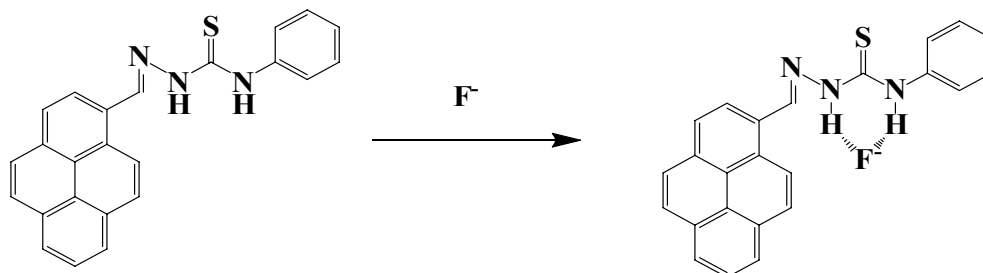


Figure 3. The Job's plot method of pyrene based molecule + F^- in DMSO. The total concentration of pyrene based molecule and F^- was 10 μ M.



Scheme 2. The probable mechanism of pyrene based molecule + F^- .

Therefore, probable mechanism of pyrene based molecule + F^- was proposed in Scheme 2. The thiourea functional group has been reported as the function of interaction with fluoride ion⁶⁻¹². According to these references, NH- fragments in thiourea moiety is possible to make the coordination bond with F^- .

We found that the change of optical properties was induced by the interaction between pyrene based molecule and F^- from the above results. In this regard, the band gap energy and HOMO/LUMO energy potential levels of pyrene based molecule before and after interacting with F^- were investigated using absorption measurement, cyclic voltammogram and computational calculation.

First, the band gap energy was obtained using absorption measurement in Figure 4 (a) and (b). These values were calculated by following equation (1)^{4,15-18}.

$$eV = 1240 / \lambda \text{ from absorption edge} \dots\dots\dots (1)$$

In Figure 4 (a) and (b), 2.89eV and 2.31eV were obtained for band gap energy values for respective pyrene based molecule and pyrene based molecule + F^- . After addition of F^- to pyrene based molecule, the band gap energy value decreased about 0.58eV. The result showed that interaction between pyrene based molecule and F^- may affect to band gap energy values.

To determine HOMO/LUMO values using onset and peak potentials, the cyclic voltammogram spectra was investigated. As shown in Figure 5 (a) and (b), only reduction peak and onset points were observed.

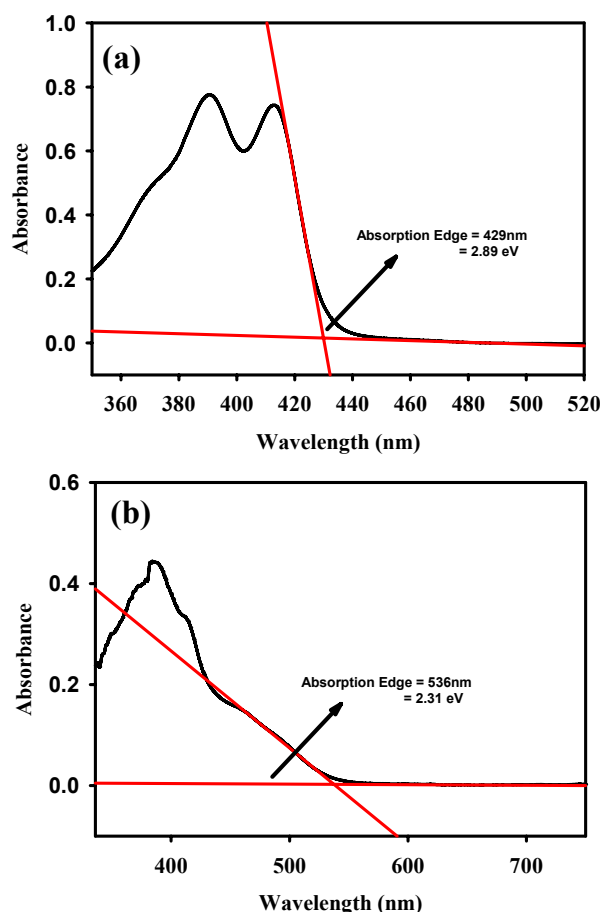


Figure 4. UV-Vis band gap measurements : (a) pyrene based molecule (10 μ M), (b) pyrene based molecule (10 μ M) + F⁻ (30 μ M) in DMSO.

Comparing these spectra, different potential positions and shapes were found and indicated that interaction between pyrene based molecule and F⁻ may affect to the electrochemical behavior.

$$\text{LUMO (eV)} = -4.8 - (E_{\text{peak or onset}} - E_{1/2(\text{Ferrocene})}) \cdots (2)$$

To calculate LUMO values using these obtained peak and onset potential values, the following equation (2) was used. 0.42V was applied for $E_{1/2(\text{Ferrocene})}$ value in this equation^{4,15-18}. LUMO values using onset and peak potentials for pyrene based molecule were obtained for -3.37eV and -3.13eV, respectively. However, pyrene based molecule + F⁻ showed different results. -3.36eV and -3.25eV were obtained using each onset and peak potential value.

In addition, the computational calculation method to the investigated HOMO/LUMO energy levels and

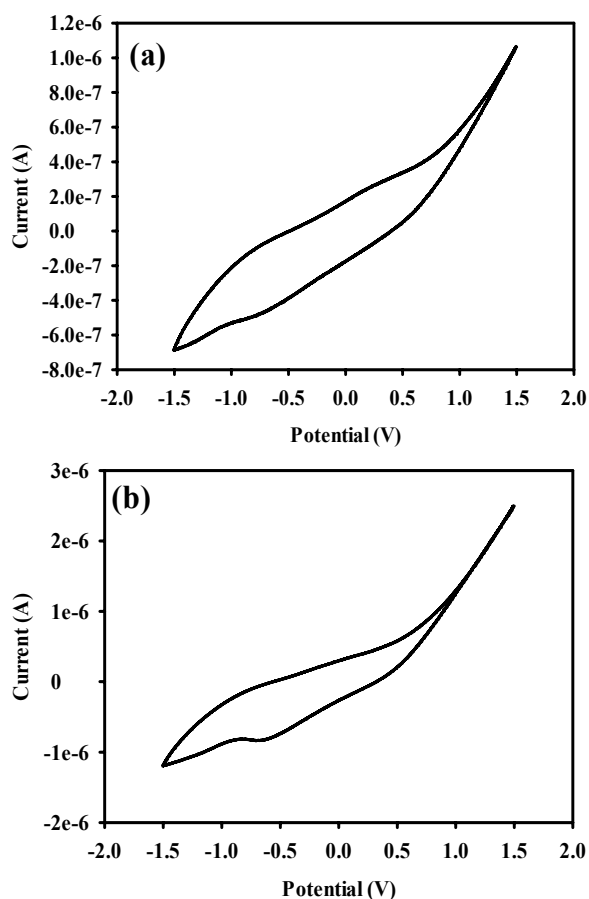


Figure 5. Cyclic voltammograms : (a) pyrene based molecule (50 μ M), (b) pyrene based molecule (50 μ M) + F⁻ (50 μ M) in DMSO. Tetrabutylammonium perchlorate was added for electrolyte.

electron distributions about the probable mechanism of respective pyrene based molecule and pyrene based molecule + F⁻ using *Material studio 4.3* package. This program is the quantum mechanical code using density functional theory. Perdew-Burke-Ernzerhof function of generalized gradient approximation level with double numeric polarization bases set was used to calculate the energy level of the frontier molecular orbitals¹⁹⁻²¹. The electron distributions of HOMO/LUMO states were simulated in Figure 6. In HOMO states, most of electrons were existed in thiourea moiety before and after interaction of F⁻. However, the electrons were moved to pyrene fluorophore in LUMO states. This result indicated that the pyrene based molecule has an intra-molecular charge transfer system.

To compare experimental and simulated values in detail, all the values were categorized in Table 1.

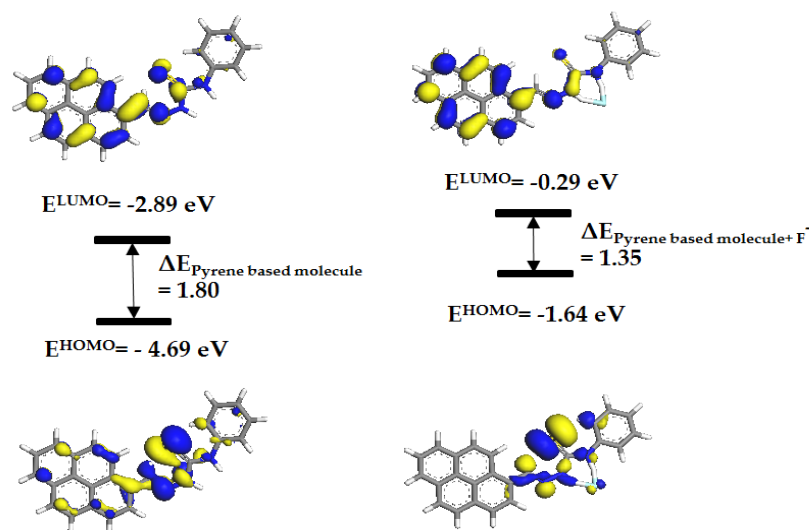


Figure 6. HOMO/LUMO energy levels and electron distributions for pyrene based molecule and pyrene based molecule + F⁻.

Table 1. HOMO/LUMO and band gap energy potential

Type	Onset (eV)			Peak (eV)			Computational calculations (eV)		
	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE	HOMO	LUMO	ΔE
Molecule	-6.26	-3.37	2.89	-6.02	-3.13	2.89	-4.69	-2.89	1.80
Molecule + F ⁻	-5.67	-3.36	2.31	-5.56	-3.25	2.31	-1.64	-0.29	1.35

Respective HOMO/LUMO values showed much difference between experimental and simulated values. However, band gap energy values were relatively closer than HOMO/LUMO values. In particular, the band gap energy value decreased when pyrene based molecule interacted with F⁻. This result is another evidence to understand the effect of interaction between pyrene based molecule and F⁻ for energy potential levels.

4. Conclusions

In this study, pyrene based molecule was synthesized through the reaction of through the reaction of pyrene -1-carboxaldehyde and 4-phenylthiosemicarbazide. The optical properties were investigated and showed the absorption and fluorescence spectra changes before and after addition of F⁻ to pyrene based molecule. In this regard, absorption measurements, cyclic voltammogram and computational method were progressed to investigate the relationship between interaction between pyrene based molecule + F⁻ and its effect of energy

potential levels. The HOMO/LUMO values and electron distributions were determined and compared. Through all the results, interaction between pyrene based molecule and F⁻ can affect to its optical properties and energy potential levels. In addition, the pyrene based molecule also showed the character of the intra charge molecular transfer.

Acknowledgement

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